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351/NF/03**We claim:**

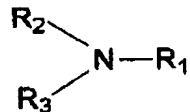
1. A process for preparing dioxy-functionalized propane compounds of formula X-CH₂-CH(Y)-CH₂-Z wherein X = R-C(=O)-O- or H or -OH, Y and Z = -H or -OH or -C(=O)H, and wherein at a time only one of X, Y and Z is -H, which comprises:
 - (a) contacting a vinyl carboxylate with carbon monoxide and hydrogen in a solvent in the presence of transition metal catalyst, to obtain an intermediate product mixture comprising of 3-carboxypropanal and 2-carboxypropanal;
 - (b) adding water to the intermediate product mixture of 3-carboxypropanal and 2-carboxypropanal to extract the carboxypropanals into water to obtain an aqueous phase comprising of carboxypropanals and an organic phase comprising of transition metal catalyst and separating the aqueous phase from the organic phase;
 - (c) contacting the aqueous phase comprising of carboxypropanals with hydrogen in presence of a heterogeneous hydrogenation catalyst to obtain a hydrogenation product mixture comprising of 3-carboxypropanol and 2-carboxypropanol in aqueous phase and separating the hydrogenation catalyst from the aqueous phase;
 - (d) contacting the aqueous phase obtained in (c) comprising of carboxypropanols with a hydrolysis catalyst at a temperature within the range of 30°C to 120°C at least during a portion of a hydrolysis step to provide a product mixture comprising of 1, 3- and 1, 2-propanediol and a corresponding carboxylic acid;
 - (e) separating and recovering carboxylic acid, 1, 3- and 1, 2-propanediols from the aqueous mixture by distillative separation.
2. A process as claimed in claim 1 wherein the organic phase obtained in step (b) is recycled to step (a).
3. A process as claimed in claim 1 wherein step (a) above is carried out in the presence of a promoter or a ligand and at a temperature in the range of 50°C to 140°C and a pressure in the range of 500 psi to 5000 psi.
4. A process as claimed in claim 1 wherein step (b) is carried out at a temperature of not more than 100°C.
5. A process as claimed in claim 1 wherein the aqueous phase of carboxypropanals is separated from the organic phase comprising transition metal by phase separation.
6. A process as claimed in claim 1 wherein step (c) is carried out at a minimum temperature of 40°C and at least for a period of 30 min, while optionally increasing the reaction temperature to 80°C and hydrogen pressure of at least 200 psi.

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7. A process as claimed in claim 1 wherein the aqueous phase comprising carboxypropanols in step (c) is separated from the hydrogenation catalyst by filtration, decantation or centrifugation.
8. A process as claimed in claim 1 wherein the transition metal catalyst used in step (a) comprises a Group VIII transition metal catalyst selected from the group consisting of rhodium, ruthenium, iridium, cobalt, palladium and nickel.
9. A process as claimed in claim 1 wherein the transition metal catalyst is selected from the group consisting of cobalt carbonyl, rhodium carbonyl and any mixture thereof.
10. A process as claimed in claim 1 wherein the transition metal catalyst is modified by a ligand comprising an organic compound of a Group V element selected from the group consisting of triaryl-phosphines, trialkyl-phosphines, arsines and amines.
11. A process as claimed in claim 1 wherein the catalyst of step (a) is used in the form of metal, supported metal, hydroxide, oxide, carbonate, sulfate, acetylacetone, salt of a carboxylic acid, and an aqueous salt solution.
12. A process as claimed in claim 1 wherein the catalyst of step (a) is used directly in the form of cobalt carbonyl or rhodium carbonyl selected from the group consisting of dicobalt octacarbonyl, cobalt hydridocarbonyl, tetrarhodium dodecacarbonyl, and dicarbonylacetylacetatonatorrhodium.
13. A process as claimed in claim 1 wherein the catalyst of step (a) is used in the form of an organometallic complex of the transition metals and ligands selected from the group consisting of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and $\text{HCo}(\text{CO})_3(\text{PBu}_3)$.
14. A process as claimed in claim 1 wherein the catalyst of step (a) in carbonyl form is formed in situ through the reaction of the metal with H_2 and CO, and at a temperature of at least 50°C and a carbon monoxide partial pressure of at least about 100 psi.
15. A process as claimed in claim 1 wherein the temperature for in situ catalyst formation is in the range of 120°C to 200°C, and the CO pressures is at least about 500 psi.
16. A process as claimed in claim 1 wherein high surface area activated carbon or zeolite containing or supporting platinum or palladium metal are added to the reactor to form cobalt carbonyl from noncarbonyl precursors.
17. A process as claimed in claim 1 wherein the amount of transition metal present in the reaction mixture is in the range of 0.01 to 1 wt% based on weight of reaction mixture.
18. A process as claimed in claim 17 wherein the amount of transition metal present in the reaction mixture is in the range of 0.05 to 0.3 wt%, based on weight of reaction mixture.

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19. A process as claimed in claim 1 wherein the cobalt catalyst is present in the range of 0.005 to 0.5 wt% based on the weight of the reaction mixture.
20. A process as claimed in claim 19 wherein the cobalt catalyst is present in the range of 0.01 to 0.1 wt% based on the weight of the reaction mixture.
21. A process as claimed in claim 1 wherein the hydroformylation catalyst in step (a) comprises a cobalt complex selected from the group consisting of cobalt acetate, cobalt hydroxide, cobalt oxide, cobalt carbonate, cobalt sulfate, cobalt acetylacetone, cobalt carboxylate, dicobalt octacarbonyl, cobalt hydridocarbonyl and $\text{HCo}(\text{CO})_3(\text{PBu}_3)$.
22. A process as claimed in claim 1 wherein the hydroformylation catalyst in step (a) comprises a rhodium complex selected from the group consisting of rhodium acetate, rhodium hydroxide, rhodium oxide, rhodium carbonate, rhodium sulfate, rhodium acetylacetone, rhodium carboxylate, tetrarhodium dodecacarbonyl, dicarbonylacetyleacetato rhodium and an organometallic complexes of the transition metals and a ligand comprising $\text{HRh}(\text{CO})(\text{PPh}_3)_3$.
23. A process as claimed in claim 21 wherein the cobalt carbonyl catalyst includes a lipophilic amine promoter in an amount effective to promote the hydroformylation reaction to acetoxypropanals.
24. A process as claimed in claim 21 wherein the lipophilic amine promoter is present in an amount in the range of 0.01 to 9 moles based on cobalt.
25. A process as claimed in claim 24 wherein the lipophilic amine promoter is present in an amount in the range of 0.6 to 3 moles based on cobalt.
26. A process as claimed in claim 24 wherein the lipophilic amine is of the formula:



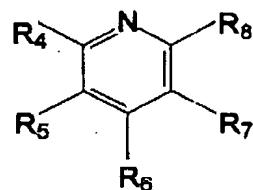
wherein each of R_1 , R_2 and R_3 are independently selected from hydrogen and/or unsubstituted and non-interfering substituted $\text{C}_1\text{-C}_{23}$ hydrocarbons.

27. A process as claimed in claim 24 wherein the amine is selected from the group consisting of dimethyl amine, diethyl amine, n-butyl amine, di-n-butyl amine, sec-butyl amine, di-sec-butyl amine, n-hexyl amine, di-n-hexyl amine, octyl amine, di(2-ethylhexyl) amine, dodecyl amine, steryl amine, allyl amine, diallyl amine, crotyl amine, dicrotyl amine, cyclopentyl amine, dicyclopentyl amine, dicyclohexyl amine, benzyl amine, dibenzyl amine, phenyl ethyl amine, diphenyl amine, cinnamyl amine,

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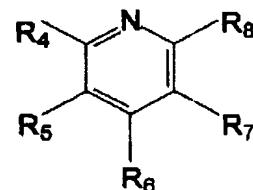
dicinnamyl amine, aniline, o-, m- and p- toluidines, 1,2,3-xylidine, 1,2,4- xylidines, 1,3,5-xylidines, 1,3,4-xylidine, mesidine, pacudocumidine, monoethyl aniline, benzyl aniline, pyrrole, guanidine, triethyl amine, trimethyl amine, tributyl amine, trihexyl amine, triphenyl amine and diphenyl methyl amine.

28. A process as claimed in claim 24 wherein in another embodiment of the invention, two of R₁, R₂, and R₃ form a ring structure such as Pyridine and substituted pyridines of the formula



wherein each of R₄, R₅, R₆, and R₇ is independently selected from hydrogen and C₁-C₂₅ hydrocarbons

29. A process as claimed in claim 24 wherein two of R₁, R₂, and R₃ form a ring structure such as Pyridine and substituted pyridines of the formula



wherein each of R₄, R₅, R₆, and R₇ is independently selected from hydrogen and C₁-C₂₅ hydrocarbons.

30. A process as claimed in claim 24 wherein the promoter is a non-chelating amine of a conjugate acid (pKa about 5-11) selected from the group consisting of tertiary amines including dimethyldodecylamine, pyridine, 4-(1-butylpentyl)pyridine, quinoline, isoquinolein, lipdine and quinaldine.

31. A process as claimed in claim 30 wherein the promoter is pyridine.

32. A process as claimed in claim 24 wherein the vinyl carboxylate is of the formula R-C(=O)-O-CH=CH₂ where R is an organic group selected from the group consisting of an alkyl group, aryl group, an organic hydrocarbyl radical comprising an alkyl group with 1 to 6 carbon atoms, phenyl and tolyl.

33. A process as claimed in claim 24 wherein the vinyl carboxylate is a residue of an organic acid selected from the group consisting of formic acid, acetic acid, propionic acid and benzoic acid.

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34. A process as claimed in claim 24 wherein the vinyl carboxylate is vinyl acetate.
35. A process as claimed in claim 24 wherein the vinyl carboxylate is present at the start of the hydroformylation step in a concentration in the range of 0.01% to 95% by weight based on the total weight of reactants, catalyst and liquid medium present
36. A process as claimed in claim 24 wherein the vinyl carboxylate is present at the start of the hydroformylation step in a concentration in the range of 0.5% to 75%, by weight based on the total weight of reactants, catalyst and liquid medium present.
37. A process as claimed in claim 24 wherein the carboxylic acid, corresponding to the vinyl carboxylate used, recovered in step (e) is recycled to produce the vinyl carboxylate starting material.
38. A process as claimed in claim 24 wherein step (a) is carried out with a cobalt/rhodium catalyst and a ligand comprising a nitrogen containing ligand selected from the group consisting of triphenyl amine, triethyl amine, tricyclohexyl amine, pyridine and substituted pyridine.
39. A process as claimed in claim 38 wherein the ligand is 4-methyl pyridine.
40. A process as claimed in claim 24 wherein the ligand used with the cobalt/rhodium catalyst in step (a) comprises a phosphorous, arsine or stilbene containing ligand selected from the group consisting of triphenyl phosphine, tributyl phosphine, triphenyl arsine and triphenyl stilbene.
41. A process as claimed in claim 24 wherein the ligand used with the cobalt/rhodium catalyst in step (a) comprises a polydentate ligand selected from the group consisting of diphenyl phosphinoethane, diphenyl phosphinopropane, diphenyl phosphinobutane, diphenyl phosphinopentane, bipyridine and terpyridine.
42. A process as claimed in claim 24 wherein the cobalt/rhodium catalyst used in step (a) is used along with a promoter comprising a quaternary ammonium salt selected from the group consisting of tetra alkyl ammonium halide and tetra alkyl ammonium hydroxide.
43. A process as claimed in claim 24 wherein the promoter used in step (a) along with cobalt / rhodium catalyst comprises a quaternary phosphonium salt selected from the group consisting of tetra alkyl phosphonium halide and tetra alkyl phosphonium hydroxide.
44. A process as claimed in claim 24 wherein the ligand used in step (a) along with cobalt/rhodium catalyst comprises an optically active ligand in order to obtain optically active - chiral 2-acetoxy propanal.

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45. A process as claimed in claim 24 wherein the solvent used in step (a) comprises an aliphatic hydrocarbon selected from the group consisting of hexane, cyclohexane and decane.
46. A process as claimed in claim 24 wherein the solvent of step (a) comprises an aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene.
47. A process as claimed in claim 24 wherein the solvent of step (a) is toluene.
48. A process as claimed in claim 24 wherein the solvent used in step (a) is selected from the group consisting of high molecular weight ethers, polyethers comprising glycol polyethers, and cyclic ethers comprising diethyl ether, methyl-t-butyl ether, ethyl-t-butyl ether, preferably, methyl t-butyl ether.
49. A process as claimed in claim 24 wherein the solvent used in step (a) is selected from the group consisting of amides and sulpholanes.
50. A process as claimed in claim 24 wherein the solvent used in step (a) comprises a chlorinated solvent selected from the group consisting of dichloromethane, dichloroethane, chlorobenzene and dichlorobenzene.
51. A process as claimed in claim 24 wherein the solvent used in step (a) is selected from the group consisting of an alcohol, a ketone, an ester and mixtures thereof.
52. A process as claimed in claim 24 wherein the solvent used in step (a) comprises a solvent blend selected from the group consisting of tetrahydrofuran/toluene, tetrahydrofuran/heptane, and t-butylalcohol/hexane.
53. A process as claimed in claim 24 wherein the solvent used in step (a) is a mixture of a non-miscible hydrocarbon solvent comprising toluene and an aqueous solvent comprising water, enabling the separation of products obtained in aqueous phase during the course of the reaction.
54. A process as claimed in claim 24 wherein the hydroformylation reaction in step (a) is carried out at a temperature of about 140°C, preferably 90°C to 130°C, most preferably 100°C to 120°C, and at a pressure within the range of about 500 to about 5000 psi, preferably about 1000 to about 3500 psi.
55. A process as claimed in claim 24 wherein the hydroformylation reaction in step (a) is carried out at a temperature in the range of 90°C to 130°C.
56. A process as claimed in claim 24 wherein the hydroformylation reaction in step (a) is carried out at a temperature in the range of 100°C to 120°C.
57. A process as claimed in claim 24 wherein the hydroformylation reaction in step (a) is carried out at a pressure in the range of 500 to 5000 psi.

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58. A process as claimed in claim 24 wherein the hydroformylation reaction in step (a) is carried out at a pressure in the range of 1000 to 3500 psi.
59. A process as claimed in claim 24 wherein step (a) is carried out at temperature in the range of 90 to 120°C.
60. A process as claimed in claim 24 wherein the hydrogen and carbon monoxide are introduced in the reaction in a molar ratio in the range of 1:2 to 8:1, preferably 1.5:1 to 5:1.
61. A process as claimed in claim 24 wherein CO and H₂ are used in step (a) in a ratio in the range of 4:1 to 1:4.
62. A process as claimed in claim 24 wherein the rhodium catalyzed hydroformylation of vinyl carboxylate includes a phosphorous, nitrogen, arsine or stilbene containing ligand selected from the group consisting of monodentate ligands such as triphenyl phosphine, tributyl phosphine, triphenyl amine, triphenyl arsine, triethyl amine, tricyclohexyl amine, pyridine, substituted pyridines such as 4-methyl pyridine and polydented ligands such as diphenyl phosphinoethane, diphenyl phosphinopropane, diphenyl phosphinobutane, diphenyl phosphinopentane, bipyridine, terpyridine.
63. A process as claimed in claim 24 wherein the reaction is carried out in the presence of an optically active ligand in order to obtain optically active 2-acetoxypropanal.
64. A process as claimed in claim 24 wherein the ratio of the ligand is at least one equivalent of ligand per mole of metal in the catalyst.
65. A process as claimed in claim 24 wherein water is added in step (b) as to provide a water: hydroformylated mixture ratio in the range of 1:1 to 1:20, preferably 1:5 to 1:15.
66. A process as claimed in claim 24 wherein the water extraction is carried out at a temperature in the range of 25°C to 55°C and under 50 to 300 psi carbon monoxide.
67. A process as claimed in claim 24 wherein the hydroformylation is carried out using reverse biphasic system in continuous mode, wherein water is added as a co-solvent during the hydroformylation in step (a) to create a separate phase thereby enabling extraction during the hydroformylation step.
68. A process as claimed in claim 24 wherein the aqueous extract containing acetoxypropanals obtained in step (c) is passed through a bed of purifying agents.
69. A process as claimed in claim 68 wherein the purifying agent is purifying carbon.
70. A process as claimed in claim 24 wherein the hydrogenation of the acetoxypropanals in step (c) to acetoxypropanols is carried out in aqueous solution at an elevated

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temperature of at least about 40°C, generally in the range of 50°C to 175°C and under a hydrogen pressure of at least about 100 psi generally in the range of 200 to 2000 psi.

71. A process as claimed in claim 24 wherein the hydrogenation is carried out in the presence of a hydrogenation catalyst selected from the group consisting of group VIII metals based catalysts selected from Ni, Co, Ru, Pt, Pd based catalysts and Cu, Zn, Cr, Au based catalysts including bulk, supported and fixed bed forms.
72. A process as claimed in claim 24 wherein the hydrogenation catalyst of step (c) is a supported catalyst selected from the group consisting of ruthenium, nickel, cobalt, platinum and palladium catalyst.
73. A process as claimed in claim 24 wherein the temperature of the hydrogenation reaction of step (c) is in the range of 40°C to 90°C.
74. A process as claimed in claim 24 wherein the hydrogenation catalyst separated in step (c) is recycled.
75. A process as claimed in claim 24 wherein the hydrogenation reaction of step (c) is carried out in a continuous manner.
76. A process as claimed in claim 24 wherein the hydrogenation catalyst in step (c) is Ru/Al₂O₃.
77. A process as claimed in claim 24 wherein the hydrogenation catalyst in step (c) is Raney Ni.
78. A process as claimed in claim 24 wherein the hydrogenation is carried out in the same solvent of hydroformylation, after removal of the hydroformylation catalyst by complexation or using activated charcoal / activated silica.
79. A process as claimed in claim 24 wherein the hydrogen pressure of step (c) is in the range of 200 psig to 800 psig.
80. A process as claimed in claim 24 wherein the hydrolysis of step (d) is carried out in the presence of an acid or base catalysts for ester hydrolysis, selected from the group consisting of mineral acids, sulphonic acids, ion exchange resins, solid acids comprising ZSM-5 etc., heteropolyacids, carboxylic acids, sodium hydroxide and potassium hydroxide.
81. A process as claimed in claim 24 wherein the temperature of the hydrolysis reaction for an ion exchange resin catalyzed hydrolysis reaction is in the range of from room temperature to 120°C, preferably from 50°C to 80°C.

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82. A process as claimed in claim 24 wherein the ion exchange resin used is Amberlite IR-120 cation exchange resin for the hydrolysis of a mixture of 2- and 3-acetoxypropanols to 1,2- and 1,3-propanediols.
83. A process as claimed in claim 24 wherein the hydrolysis in step (d) is carried out with 10% HCl
84. A process as claimed in claim 24 wherein the hydrolysis step (d) is carried out in a continuous manner.
85. A process as claimed in claim 24 wherein the hydrolysis catalyst from step (d) is activated and recycled.
86. A process as claimed in claim 24 wherein the carboxylic acid, 1,3-propanediol, and 1,2-propanediol formed are separated by fractional distillation in step (e).
87. A process as claimed in claim 24 wherein the hydrolysis in step (d) is carried out before hydrogenation of step (c) in order to obtain 2- and 3- hydroxy propanal.